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(57) Abstract

The invention provides a method for the continuous manufacture of ferritic stainless steel bands suitable for use in environments with frequent changes in temperature. It has been found preferable to have such band longitudinally displaced through a coating chamber wherein the band is provided with a coating of aluminum that is deposited thereon by means of physical vapor deposition technology during a time period sufficient so that aluminum becomes evenly distributed in the ferrite, after which a homogenization occurs at 950-1150 °C.

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METHOD OF MANUFACTURING FERRITIC STAINLESS FeCrAl-STEEL STRIPS

The present invention relates to a new method of making high temperature resistant FeCrAl-steel strip from ferritic (FeCr) stainless steel by using physical deposition technology which usually is called "physical vapour deposition" (PVD)-technique. Steel strips rich in aluminum are used in applications where there is a need of high temperatures and quick change in temperature. One example is thin foils for metallic catalytic converters where aluminum is used to form oxides that protect the steel surface from corrosive attacks. One great advantage of the invention is the increased flexibility in varying the analysis of said steel, primarily in regard of the aluminum content.

It is prior art to use FeCrAl-alloys for heat resistant applications such as purification of automobile gases by using metallic catalytic converters. Aluminum is added to the steel to form aluminum oxide which is one of the most stable oxides having low speed of oxygen diffusion. Therefor, the aluminum oxide provides a good protection against corrosion at high temperatures in oxidation atmosphere. Those alloys are difficult to manufacture by conventional steel-making from scrap-based metallurgy via casting, hot rolling and cold rolling. Inevitably both macroscopic and microscopic inclusions will be formed, mainly aluminum-based which will complicate their manufacture and contribute to less efficiency primarily when cold rolling the material down to its final dimension. Intermetallic phases will be formed at 450-500°C and those precipitations will reduce the toughness of the material and make the steel brittle. This means that the heat treatment steps involved in the manufacture must be carried out very carefully. i.e. the material must be quenched below that area where intermetallic phases are being formed. It is established that conventional manufacturing technology puts a limitation to the aluminum content at maximum 6 % in order to minimize such process problems.

There are other methods available for the making of this type of material and one method includes rolling a ferritic stainless steel jointly with an aluminum foil (US-Patent 5,366,139 and 5,447,698). A ferritic chromium steel is rolled to suitable band thickness after which said band is rolled jointly with a surrounding aluminum foil

to a final thickness. Such cold rolled composite material consists of three layer that is being heat treated to obtain a homogenous material with aluminum evenly distributed in the ferritic matrix.

Another variant includes dipping the steel band into a bath of liquid aluminum or an aluminum alloy (US-Patent 3,907,611, 3,394,659 and 4,079,157). This method, however, is complex and it is difficult to control the process parameters. This causes large manufacturing costs which are not commercially feasible.

It is a primary object of the invention to provide a new method for the manufacture of high temperature resistant FeCrAl-bands which is not connected with same limitations in regard of Al-content as associated with conventional methods. It is another purpose to provide a method that enables continuous production "on-line" at very moderate cost levels. Such object is achieved by means of a method according to the invention such as outlined in the appending patent claim 1.

The invention will now be described by reference to some examples by referring to the attached drawings, in which

Fig. 1 is a principal sketch of the physical deposition method for applying aluminum.
Fig. 2 is an example of a continuous manufacture line for making FeCrAl-bands.
Fig. 3 is a flow chart of the manufacture according to one embodiment of the invention, and
Fig. 4 is a flow chart of another alternative manufacturing sequence in accordance with the invention.

According to the invention the raw material shall be a ferritic stainless chromium steel with suitable additive components so as to increase high-temperature strength of such material, including rare earth metals such as cerium, lanthanum or yttrium, which material shall be manufactured by scrap-based metallurgy and subjected to hot rolling down to smallest possible strip thickness. The material is then subjected to cold rolling to a suitable dimension after which the material is subject of aluminum deposition by

Physical Vapour Deposition (PVD)-technology. The steel strip could be coated with aluminum after rolling to final dimension, or coated at an intermediate dimension after which such Al-coated strip becomes subject of further working to its final cold rolled thickness. In order to ensure that a fully homogenous strip with aluminum evenly distributed in the ferrite is obtained it is necessary to make said strip subject of heat treatment at about 950°C up to about 1150°C during a suitable time period.

Aluminum will be diffused into the ferritic steel, and the time period required for this even distribution depends of those time-temperature conditions that are selected and the thickness of said ferritic Cr-steel. In accordance with one process embodiment the heat treatment is made "on-line" in association with the PVD-equipment before the strips are coiled. As a result of such fabrication a homogenous steel strip containing 70-75 wt-% Fe, 15-25 wt-% Cr and 5-10 wt-% Al can be made thanks to this sequence of process steps.

Many various PVD-methods are known for the use of different types of vapor deposition sources that enable the decomposition of aluminum into atoms. Thermal vaporization or evaporation are very suitable technologies for depositing aluminum. As exemplary methods can be mentioned heating by resistivity, by electron-beam, by induction, by arc resistance or by laser. Evaporation by electron-beam is a relatively simple and cheap method and can to advantage be used for the deposition of aluminum.

Fig. 1 shows schematically an equipment that includes a water-cooled copper ladle 10 in which a smelt of aluminum 11 is contained and kept at sufficient temperature, A steel band 12 of ferritic Cr-steel is longitudinally displaced above said ladle. An electron gun 13 is located on a suitable distance above the ladle 10 so as to ensure that a sufficient plasma 14a of aluminum is obtained so as to form a coating 14b on the band 12.

The equipment shown in Fig. 2 for continuous fabrication of FeCrAl-bands includes a coil 15 from which the band 12 is fed into a washing device 16 in which the band is clean-washed. The band 12 is then displaced into a sluice 17 from which the band is

then displaced into a coating chamber 18 containing the equipment shown in Fig. 1. After the band has been provided with a layer of aluminum in said chamber 18 said band is displaced into a chamber 19 for heat treatment, followed by a band cooler 20 and finally a sluice 21. After leaving this equipment the band is displaced on to a coiler 22.

Example 1

A preferred process embodiment of the invention will now be described more in detail in connection with the process flow chart as shown in Fig. 3.

Firstly, a warm band 12 of a ferritic stainless Cr-steel and with rare earth additives with a thickness of 2-2.8 mm is fabricated. The band 12 is cold rolled in several steps with a certain number of recrystallization steps between said rolling steps until a cold rolled band thickness of 30-45 μm is obtained. The first step inside the PVD-installation for Al-deposition includes washing the material in a container 16 in which de-ionized water is provided. In order to obtain 5-10 weight-% of Al both sides of the band is coated with a layer with 3-10 μm thickness of pure aluminum in the coating chamber 18. The band is subjected to heat treatment at 950-1150°C in the chamber 19 during a time period from 20 seconds up to several minutes depending upon the type of heating that is used. The heat treatment can be carried out in the same line or as subsequent steps in a continuous conveyor furnace or in a bell-type furnace. The heat treatment can also be carried out in connection with the fabrication of the catalytic converter. If the heat treatment occurs in same line as the PVD-coating step a quick heating can to advantage be carried out, for instance by induction heating or direct heating via rolls. Shape problems after annealing in the PVD-line can be avoided by subjecting the material to hot straightening after heat treatment. The band will, after passing the cooler 20, be displaced through a vacuum sluice 21 before it is being coiled on to a coiler 22.

Example 2

An alternative process embodiment will now be described in connection with the flow chart shown in Fig. 4. Firstly, a band of a ferritic Cr-steel with rare earth additives is fabricated to a band thickness of 2-2.8 mm after which it is rolled to an intermediate thickness of 0.1-0.3 mm. The band is then provided with a coating of evaporated aluminum in the chamber 18 at a thickness of 10-30 μm. The material is then feeded into the chamber 19 to be heat treated at 950-1150°C in the same line or in a subsequent process step. It is preferable to make the heat treatment in a separate process step after the PVD-coating due to thc fact that the thicker band thickness will require longer annealing times. The heat treatment will replace the ordinary recrystallization anneal that is carried out before cold rolling to final dimension. After having deposited the aluminum on to the steel band and carried out homogenization of the ferritic Cr-steel this is made subject of cold rolling to the final dimension, 30-50μm.

According to a further alternative process embodiment the homogenization for obtaining diffusion of Al into the steel band can be carried out after the material is rolled to its final dimension. The heat treatment can also be carried out in connection with the fabrication of the catalytic converter.

Thanks to the new fabrication method according to the invention it becomes possible to use an installation in which the Al-deposition of the band is made continuously at high speeds. Compared with other methods, as related before, this new fabrication method becomes price competitive. The rapid coating speed is possible by using available advanced vacuum systems which are available in combination with more tight sluices. Another advantage with this PVD-method compared with other methods is that it is possible to control the coating thickness evenly along the band with high precision.

Claims

1. Method of manufacturing high-temperature resistant ferritic Cr-steel bands, including initial fabrication of FeCr-steel with rare earth metal additives and rolling such steel into band in several steps and intermediate recrystallization anneals between said rolling steps, characterized in following steps in combination

- feeding the band into a coating chamber (18) in which aluminum (13) is deposited by physical vapor deposition technique during a time period sufficient to have Al evenly distributed in the ferrite, and

- carrying out heat treatment of said band (12) in a chamber (19) at a temperature of 950-1150°C during a time sufficient to obtain homogenization and diffusion of the aluminum into said steel band.

2. Method according to claim 1, characterized in that the band is subjected to a straightening directly after the heat treatment at 950-1150°C.

3. Method according to claim 1, characterized in that the band is coated with Al in the chamber (18) during a time sufficient to obtain a coating (13b) of 3-10 μm pure Al on each side of the band (12).

4. Method according to claim 3, characterized in that heat treatment at the temperature 950-1150°C occurs in the chamber (19) during a time of about 20 seconds.

5. Method according to claim 1, characterized in that the band before entry into the PVD-equipment is caused to pass through a zone where the band is washed in de-ionized water, and that the band is subject of hot straightening directly after the heat treatment has been completed.

6. Method according to claim 1, characterized in that the band after having passed through the PVD-equipment for Al-deposition is subjected to a homogenization treatment after which the band is cold rolled to its desired final dimension.

7. Method according to claim 6, characterized in that the band after cold rolling to its final dimension is subjected to a final recrystallization anneal.

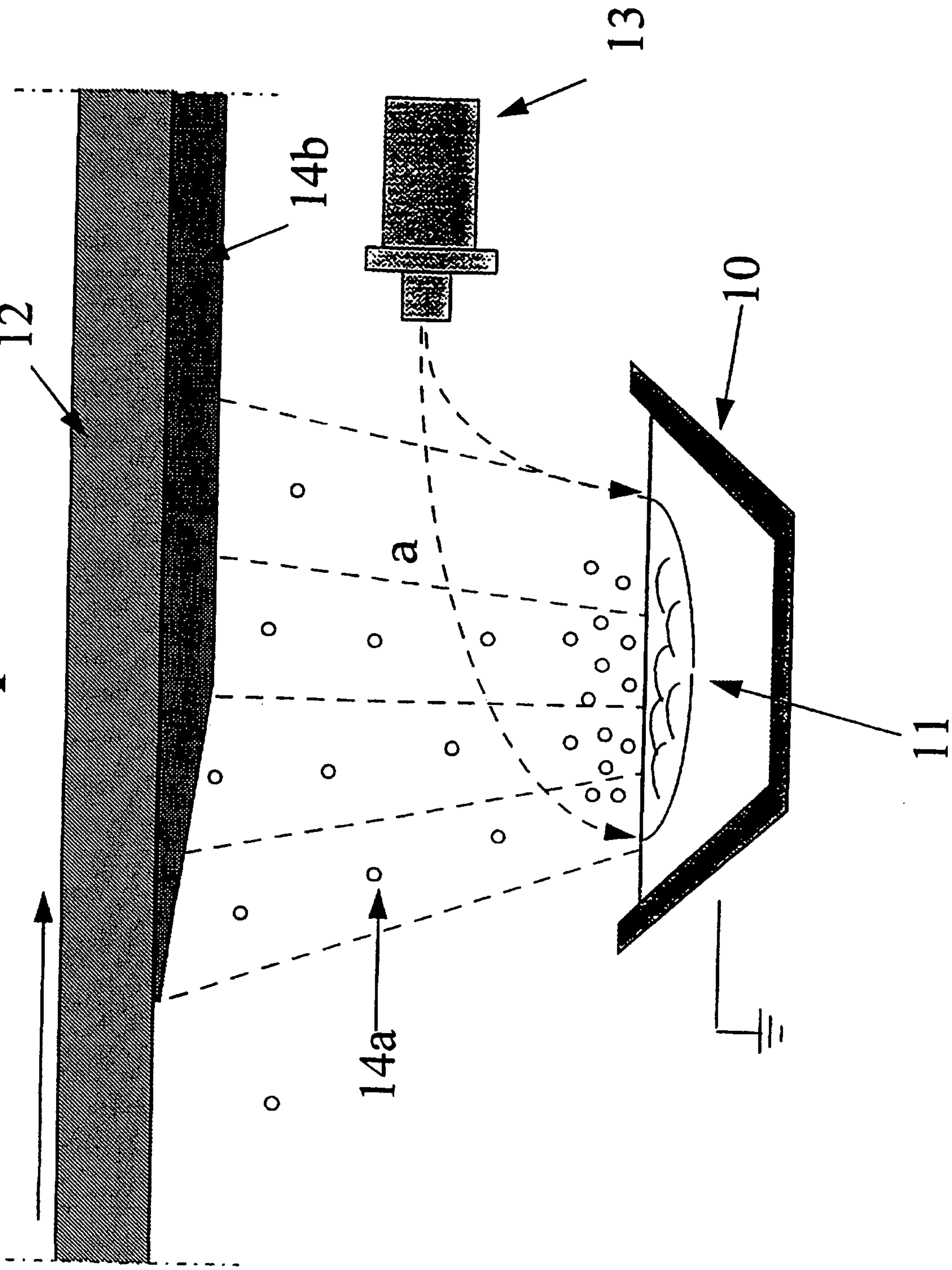


Figure 1:PVD-deposition

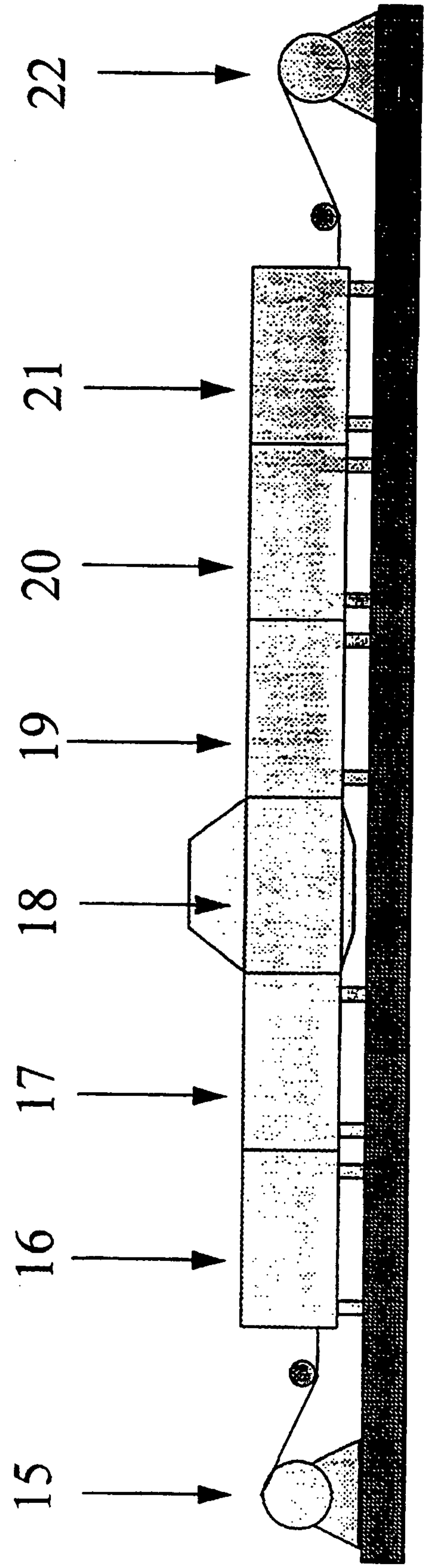


Figure 2: PVD-equipment

Figure 3: Alternative 1

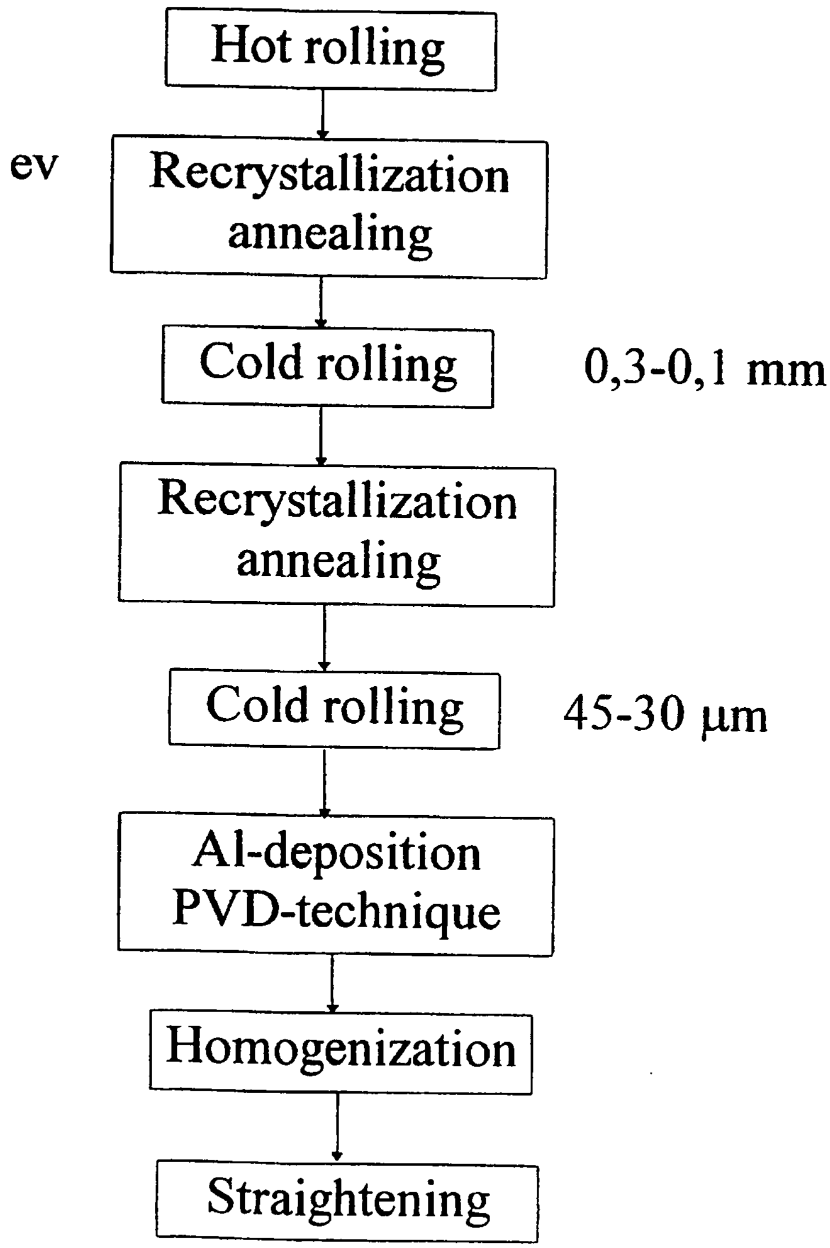
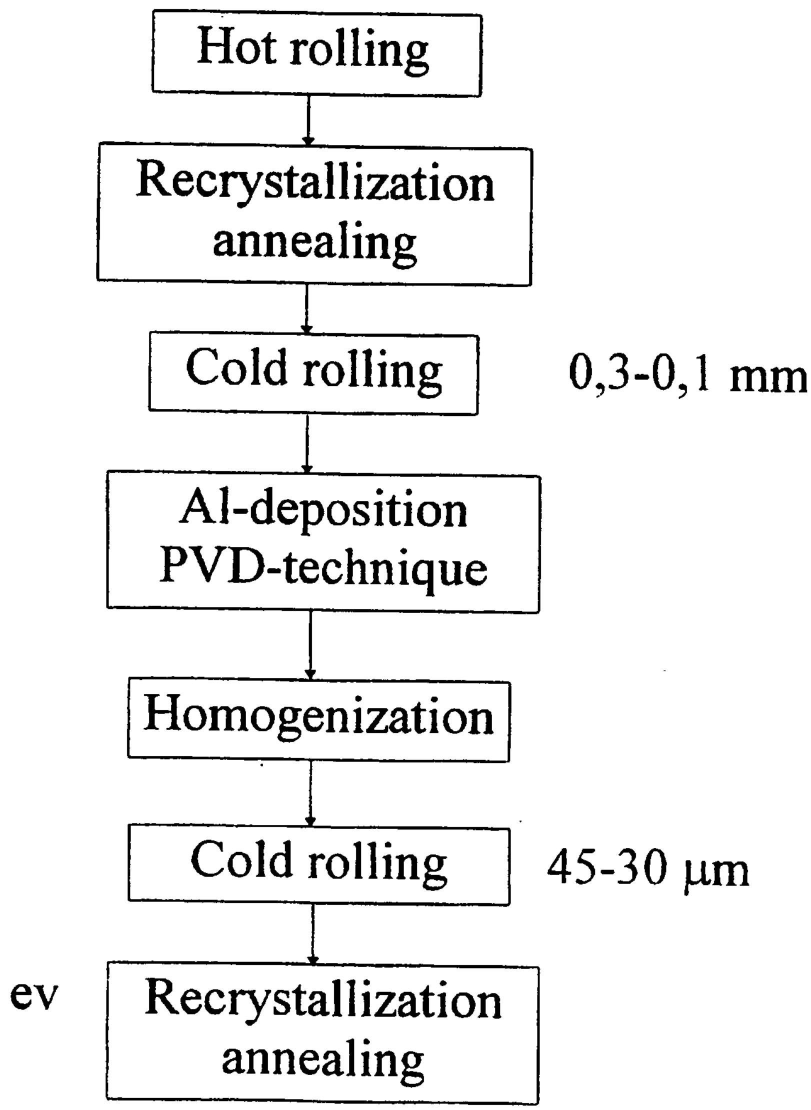


Figure 4: Alternative 2



INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C21D 8/02, C23C 14/58 // C22C 38/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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ORBIT: WPAT, USPM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5447698 A (SUNIL C. JHA ET AL), 5 Sept 1995 (05.09.95) --	1-7
A	US 3907611 A (TAKAO SASAME ET AL), 23 Sept 1975 (23.09.75) --	1-7
A	WO 9615284 A1 (CAMETOID ADVANCED TECHNOLOGIES INC.), 23 May 1996 (23.05.96) -- --------	1-7

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5447698 A	05/09/95	EP 0640390 A	01/03/95
		JP 7233427 A	05/09/95
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